U.S. Patent Application

of

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for

DISTILLATE FUEL COMPOSITIONS FOR IMPROVED COMBUSTION AND ENGINE CLEANLINESS

FIELD

The present invention relates to a synergistic interaction between an overbased calcium sulfonate detergent and an ashless succinimide dispersant that allows for the formulation of improved distillate fuel additive packages. In addition to the metallic detergent and the ashless dispersant, the additive compositions contain an organometallic complex of manganese. Distillate fuels treated with the additive compositions exhibit improved combustion because of the detergent and the organometallic manganese compound and good fuel system cleanliness because of the detergent/dispersant interaction.

BACKGROUND

A great deal of prior art has been devoted to formulating distillate fuel additive compositions to provide environmental benefits when the fuel is combusted. Such benefits include, for example, reduced emissions of noxious pollutants such as oxides of nitrogen and particulate matter, reduced acidity of emitted particulates, and better fuel economy (which amounts to lower emissions of carbon dioxide per amount of fuel burned). The effects of these fuels on the cleanliness of fuel systems, e.g., on the buildup of carbon and lacquer on the fuel injectors found in diesel engines, has received less study.

A need exists for a distillate fuel additive composition that provides for the simultaneous achievement of improved combustion, fuel and combustion system cleanliness, improved fuel economy, and reduction in pollutant generation.

SUMMARY OF THE EMBODIMENTS

An embodiment presented herein provides a fuel additive composition comprising an organometallic manganese compound, an alkyl-substituted succinimide ashless dispersant, and an

overbased calcium sulfonate detergent of TBN above about 200. In another embodiment the TBN of the overbased calcium sulfonate is about 300.

Another embodiment provides a fuel comprising a major amount of a middle distillate fuel and a minor amount of a fuel additive composition comprising an organometallic manganese compound, an alkyl-substituted succinimide ashless dispersant, and an overbased calcium sulfonate detergent of TBN above about 200.

Accordingly, in one example herein is provided a method of for improving the cleanliness of a fuel intake systems by use in the fuel intake system of a fuel containing a fuel additive composition comprising an organometallic manganese compound, an alkyl-substituted succinimide ashless dispersant, and an overbased calcium sulfonate detergent of TBN about 300.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

DETAILED DESCRIPTION OF EMBODIMENTS

In one embodiment is provided herein distillate fuel additive compositions for use in distillate fuels that provide enhanced fuel combustion and, at the same time, superior cleanliness of fuel intake systems. Distillate fuels are defined herein as petroleum-based hydrocarbon fuels boiling in the range of about 140-360°C [284-680°F] and encompass diesel and biodiesel fuels, jet fuels, marine fuels and home heating oils. Distillate fuels containing the additive compositions of the invention show enhanced combustion characteristics.

If certain components of the additive packages described herein are present in specific proportions, fuels containing the additive packages also show excellent fuel injector cleanliness

as measured by the Cummins L10 diesel detergency test. This injector cleanliness is exhibited as an injector rating of at most 10.0 in the Cummins L10 diesel detergency test.

Other embodiments herein provide an additive composition, a distillate fuel containing the additive composition, and a method of improving the cleanliness of fuel intake systems by use of the fuel containing the additive composition.

In an embodiment, the additive composition contains at least an organometallic complex of manganese, an overbased calcium sulfonate detergent and an ashless succinimide dispersant such that when the additive composition is dissolved in a distillate fuel, the following relationship is satisfied:

$$-0.159x + 0.243y - 0.0143xy \leq -8.4$$

where

x = concentration of succinimide (in pounds per thousand barrels)

y = concentration of overbased calcium sulfonate (in PTB)

with the following limitations:

x = 20-35, preferably 25-30, and y = 10-120, preferably 30-50.

The organometallic manganese compound does not affect injector cleanliness. In an embodiment, the organometallic manganese compound may be present in the fuel at concentrations of up to about 20 PTB.

It has been discovered that the combustion-improving conventional additive packages previously known do not necessarily pass the Cummins L10 diesel detergency test (where a pass is defined as an average injector rating of 10.0 or less). To identify the components in the additive composition that affect injector ratings, an experimental design was carried out. A

synergy (i.e. a nonlinear interaction) was observed between the overbased calcium sulfonate detergent and the succinimide dispersant. This was a surprising result which is not anticipated by any prior art.

The results of the experimental design were used to generate a model for average injector rating, as follows:

$$\text{Rating} = -0.159x + 0.243y - 0.0143xy + 18.4 \qquad (1)$$

where

x = concentration of succinimide (in pounds per thousand barrels, or PTB)

y = concentration of overbased calcium sulfonate (in PTB)

Since the average injector rating must be 10.0 or lower for a pass in the Cummins L10 test, the equation becomes:

$$10.0 \geq -0.159x + 0.243y - 0.0143xy + 18.4 \qquad (2)$$

or

$$-0.159x + 0.243y - 0.0143xy \leq -8.4 \qquad (3)$$

The detergent/dispersant synergy is represented by the xy term.

The model was validated by the testing of three new formulations that satisfy the above equation:

1. x = 28 PTB, y = 32 PTB
2. x = 26 PTB, y = 40 PTB
3. x = 25 PTB, y = 48 PTB

All three formulations gave an average injector rating of below 10.0, in accordance with the model. Of course, there are an infinite number of solutions for x and y in equation 3. Examples of currently practical solutions are the following ranges:

x = 20-35, preferably 25-30

y = 10-120, preferably 30-50

The amount of organometallic manganese compound was shown to have no significant adverse effect on injector ratings and is therefore not constrained by the model represented by equation 3. As an economic matter only, the amount of manganese compound is, in an embodiment, limited to 20 PTB or less. The benefits derived from the inclusion of a manganese compound are not directly related to injector ratings, but are much more prevalent in the areas of particulate emission reduction, reduced NO_x and SO_x, reduced hydrocarbons, improved fuel economy, and combustion improvement.

Especially useful herein is methylcyclopentadienylmanganese tricarbonyl (MMT®) as the organometallic manganese compound, a succinimide prepared from 850 to 2100-MW PIBSA and a polyalkylene polyamine approximating tetraethylenepentamine in composition as the ashless dispersant, and an overbased calcium sulfonate of TBN up to about 300 as the detergent. MMT® is available from Ethyl Corporation, Richmond, VA. The diesel fuel used in the Cummins L10 study was a high-sulfur (0.4wgt % sulfur) fuel, but any diesel fuel (including low-sulfur and ultralow-sulfur fuels) may be used. A separate L10 experiment has shown that the addition of 2-ethylhexyl nitrate cetane improver to a fuel containing the inventive additive does not degrade the detergent performance.

The following examples further illustrate aspects of the present invention but do not limit the present invention.

EXAMPLES:

Since the Cummins L10 test was designed to evaluate additives and fuels for on-road use in North America, HiTEC®-4080 Fuel Additive was used in this example. This additive is Ethyl

Corporation's antifoam-free Greenburn® road diesel fuel additive package, used with a recommended treat rate of 500 ppm (w/w). The formulation is shown in Table 1.

Component	% weight	ppm component at 500 ppm total	PTB component at 500 ppm total
HiTEC® 9645	15.34	76.7	22.8
2-ethylhexanol	46.22	231.1	68.8
HiTEC® 611	32.16	160.8	47.9
HiTEC® 536	0.93	4.7	1.4
D-5021	0.97	4.9	1.5
HiTEC® 3062	4.38	21.9	6.6

Table 1. Composition of HiTEC® 4080

For the purposes of this example, the European components D-5021 (demulsifier) and HiTEC® 536 (corrosion inhibitor) were replaced with the North American components Tolad 9310 and 50% dodecenylsuccinic acid, respectively, on an equivalent weight basis. These components were held constant at the above concentrations in every test. The components expected to have significant effects on Cummins L10 ratings were HiTEC® 9645 (a succinimide-based dispersant), HiTEC® 611 (overbased calcium sulfonate) and HiTEC® 3062 (62% MMT® in aromatic solvent).

The resulting two-level, three-factor (2^3) design is shown in Figure 1; the numbers along the axes denote concentrations in PTB.

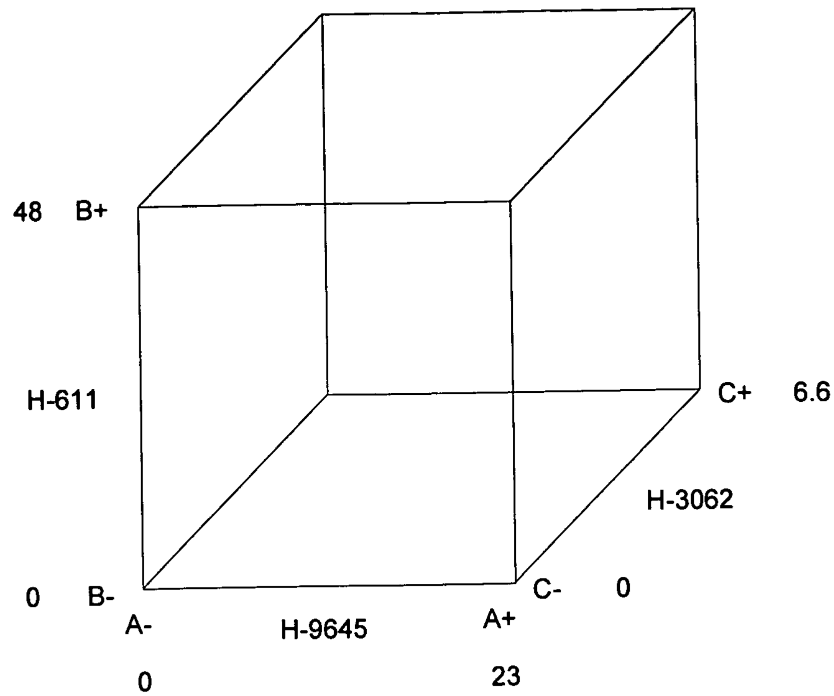

Figure 1. Experimental design for HiTEC® 4080 components

All tests were carried out in the same Cummins L10 engine and in the same batch of high-sulfur Cat 1K fuel. The test order was randomized. The results are shown in Table 2.

Test no.	PTB H-9645	PTB H-611	PTB H-3062	Avg. flow loss (%)	Avg. CRC rating
D102-97-1	0	0	6.6	3.2	19.1
D102-98-1	23	0	0	4.2	14.7
D102-99-1	23	0	6.6	2.9	15.3
D102-100-1	23	48	0	2.3	9.9
D102-101-1	0	48	6.6	8.9	34.7
D102-102-1	11.5	24	3.3	4.1	16.8
D102-103-1	0	48	0	4.0	25.9
D102-104-1	23	48	6.6	3.1	11.9
D102-105-1	0	0	0	1.9	18.2

Table 2. Cummins L10 results for H-4080 experimental design

An analysis of variance (ANOVA) on the data in Table 2 showed that average flow loss was independent of all three factors. The ANOVA for CRC rating is shown below.

Analysis of Variance for CRC

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A (H-9645)	265.651	1	265.651	29.81	0.0028
B (H-611)	28.5012	1	28.5012	3.20	0.1337
AB	124.031	1	124.031	13.92	0.0136
Total error	44.5563	5	8.91125		
Total (corr.)	462.74	8			

R-squared = 90.3712 percent
R-squared (adjusted for d.f.) = 84.5939 percent
Standard Error of Est. = 2.98517
Mean absolute error = 1.55556
Durbin-Watson statistic = 2.10796

HiTEC® 3062 and the higher-order terms AC, BC and ABC were significant at less than the 85% confidence level and are therefore excluded. The model coefficients are as follows:

Regression coeffs. for CRC

constant	= 18.4375
A (H-9645)	= -0.158696
B (H-611)	= 0.242708
AB	= -0.0142663

The regression coefficients show that HiTEC® 9645 unexpectedly decreases the CRC response (a beneficial effect, since lower CRC ratings indicate less injector depositing), while HiTEC® 611 increases the ratings. There is a significant negative interaction between HiTEC® 9645 and HiTEC® 611, meaning that the deleterious effect of HiTEC® 611 on CRC rating at low concentrations of dispersant is more than cancelled out at high dispersant concentrations. In other words, HiTEC® 611 *improves* CRC ratings when in the presence of high amounts of HiTEC® 9645. This effect is shown graphically by the interaction diagram in Figure 2. Ordinarily, a p-value of 0.13 would result in HiTEC® 611 alone being excluded from the model: this value indicates that the coefficient is different from zero only at the 87% confidence level.

However, if the model contains an interaction between HiTEC® 9645 and HiTEC® 611, the HiTEC® 611 term should also be included to preserve model hierarchy.

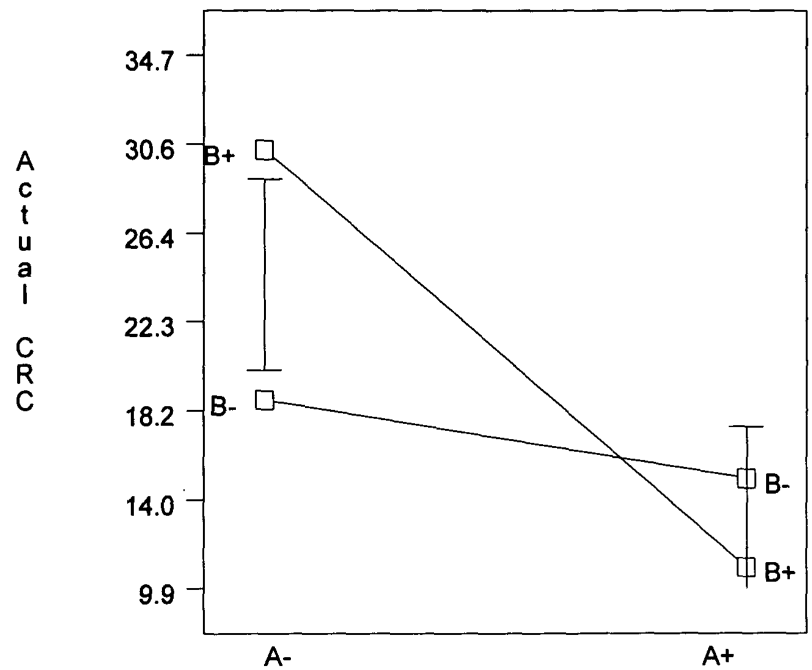

Figure 2. Interaction of A:H-9645 and B:H-611

FORMULATION OF MODIFIED DISPERSANT PACKAGES TO PASS THE CUMMINS L10 TEST

From the model developed above, it is therefore possible to adjust the components in, for example, HiTEC® 4080 in order to hit a desired CRC target. As mentioned previously, the maximum CRC rating for a Cummins L10 pass is 10.0. Constant response curves for CRC as a function of HiTEC® 9645 and HiTEC® 611 concentrations (in PTB) are shown in Figure 3.

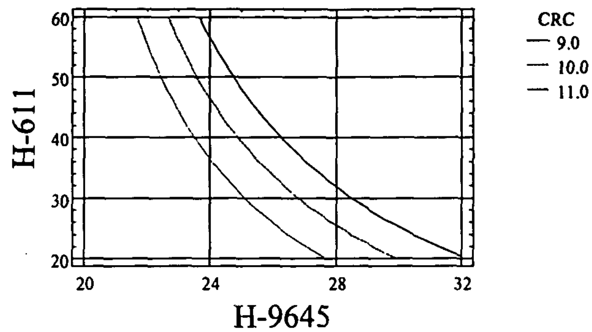

Figure 3. Contours of estimated response surfaces for CRC rating

Based on the above model for CRC, any combination of HiTEC® 9645 and HiTEC 611 to the right of the 10.0 contour (the dashed line) in Figure 3 should give a passing Cummins L10 rating. Three points were selected on the 9.0 contour (the solid line) in the L10 test. The additive combinations corresponding to these points were:

1. 28 PTB HiTEC® 9645 + 32 PTB HiTEC® 611
2. 26 PTB HiTEC® 9645 + 40 PTB HiTEC® 611
3. 25 PTB HiTEC® 9645 + 48 PTB HiTEC® 611

All three packages also contained 6.6 PTB of Ethyl's MMT® as HiTEC® 3062 plus solvent, demulsifier and corrosion inhibitor as described above. The resulting Cummins L10 data are shown in Table 3.

Modified package	Test no.	Avg. flow loss (%)	Avg. CRC rating
1	D102-107-2	2.0	8.6
2	D102-107-1	3.1	8.5
3	D102-109-1	3.3	9.9

Table 3. Cummins L10 results for modified versions of HiTEC® 4080

As expected from the above model and calculations, all three packages pass the Cummins L10 test.

A simple 2^3 experimental design has determined the quantitative effects of various components in a Greenburn® Diesel Fuel Additive package on Cummins L10 performance. It

was found that the succinimide dispersant (HiTEC® 9645) had a beneficial effect on injector ratings, while the overbased calcium sulfonate detergent (HiTEC® 611) harmed those ratings. In addition, a strong interaction between these two components was observed which reduced the undesirable effect of the detergent. MMT® (as HiTEC® 3062) had no significant effect on injector cleanliness. The model derived from the experimental design was used to formulate modified Greenburn®-type packages that passed the Cummins L10 test.

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. As used throughout the specification and claims, “a” and/or “an” may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as

exemplary only, with a true scope and spirit of the invention being indicated by the following claims.